

Novel Epoxy Particulate Composites for Mitigation of Insect Residue Adhesion on Future Aircraft Surfaces

Christopher J. Wohl,¹ Joseph G. Smith Jr.,¹ John M. Gardner,¹ Ronald K. Penner,² John W. Connell,¹ Emilie J. Siochi¹

¹NASA Langley Research Center
Hampton, VA 23681, United States of America

²Science and Technology Corporation
Hampton, VA 23666, United States of America
christopher.j.wohl@nasa.gov; emilie.j.siochi@nasa.gov

Introduction

Drag is reduced significantly for airflow over surfaces when laminar flow can be maintained over greater chord lengths, the distance from the leading edge of an airfoil.¹ However, surface imperfections, such as chipped paint, scratches, and events that change topography on a microscopic scale can introduce airflow instabilities resulting in premature transition to turbulent flow.¹ Although many of these surface imperfections can be avoided with proper maintenance, advanced materials, and advanced manufacturing practices, topographical surface anomalies arising during flight from insect impacts cannot be controlled and can influence laminar flow stability. Practical solutions to this operational challenge need to be developed for future aircraft to have full advantage of laminar flow designs that improve fuel efficiency.²

Researchers have investigated various methods to mitigate insect residue adhesion for decades.³ Although several techniques have demonstrated efficacy including mechanical scrapers, active liquid discharge systems, and sacrificial paper coatings, they have not been commercially implemented due to increased manufacturing and operational complexity, environmental impact, and weight penalties. Coatings offer a simple route for passive insect residue adhesion prevention without many of the challenges associated with maintenance of laminar flow.⁴

In our previous work, we determined that most commercially available materials were not effective at insect residue adhesion.⁵ We also identified improvements when both surface energy could be controlled by surface modifying agents and the topography could be altered through the use of micron-sized and nanometer-sized filler materials.⁶

In this work, these general principles were applied to an epoxy system to evaluate the behavior of the surface modifying agent, a fluorinated alkyl ether oligomer, on surface energy and insect residue adhesion properties.

Experimental

The epoxy system used in this work consisted of D.E.R. 331 (Dow, epoxy equivalent weight = 187.5 g/mol) and Ethacure 100 (Albemarle Corporation, amine equivalent weight = 44.57 g/mol) at a 4:5 molar ratio, respective-

ly (Figure 1). The surface modifying agent used was an amine-terminated fluorinated alkyl ether oligomer (FAE, amine equivalent weight = 435 g/mol) which was end-group functionalized from the hydroxyl-terminated oligomer PF-7002 (Omnova, hydroxyl equivalent weight = 750 g/mol).⁷ The FAE loading level was varied from 0 wt% to 5 wt% of the total epoxy mass with the amount of Ethacure 100 adjusted to maintain the 4:5 molar ratio. As an example, synthesis of a 1 wt% FAE-containing epoxy consisted of charging a small beaker with 3.3584 g of D.E.R. 331, 0.0395 g of FAE, and 0.6323 g of Ethacure. These components were stirred until uniformly mixed.

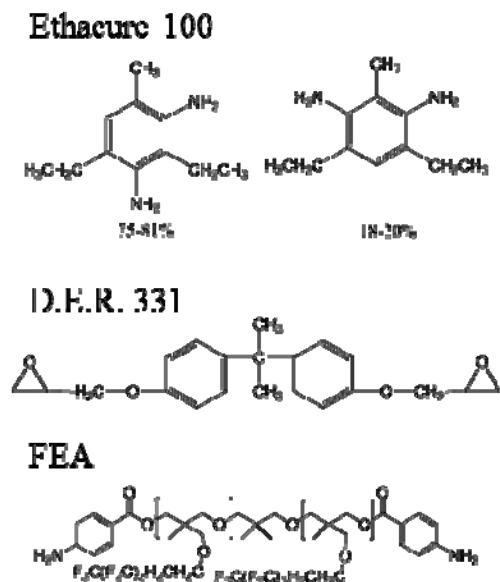


Figure 1. Materials used for epoxy synthesis.

Filler materials, MoS₂ (Sigma Aldrich, diameter < 2 μm) and fumed silica (SiO₂, Sigma Aldrich, diameter ~ 7 nm) were added to the epoxy mixture to impart topographies on the coated surfaces at loading levels from 0 wt% to 25 wt% total solids (i.e., 100 wt% to 75 wt% epoxy). Samples were fabricated for surface energy analysis and insect impact experiments by spray deposition from a methyl ethyl ketone solution (approximately 8 wt% solids) onto aluminum 1100 sheets (76.2 μm thick). This was followed by a two stage thermal cure cycle with a 2 h hold at 100 °C and a 4 h hold at 170 °C.

Contact angle measurements were collected using an FTA1000B goniometer (First Ten Angstroms). Measurements were collected using 8 μL droplets for water and ethylene glycol and 2 μL droplets for methylene iodide. Tilting axis measurements and drop shape analysis were used to determine the sessile, advancing, and receding contact angle values. A minimum of three measurements was collected with each liquid. Surface energy values, (total, polar, and dispersive) were determined via Kaelble plots.⁸ Insect impact experiments were performed in a modified bench-top wind tunnel using flightless fruit flies (*drosophila melanogaster*) that were propelled towards the investigated surface using a custom-built pneumatic delivery device.⁶ High speed photography (50,000 frames/s) documented the tests where the average insect speed was determined to be 241 km/h (150 mph). A minimum of 3 insect impacts where the insect remained intact during flight as observed via high speed photography was collected for each surface. Insect residue heights and areal coverage values were determined using an optical profilometer (Microprof 100, FRT of America). The impact sites were scanned collecting data at a resolution of 5 μm between data points and 20 μm between scan lines.

Results and Discussion

A series of FAE-containing epoxy samples was generated and evaluated to ascertain the influence of FAE and filler incorporation on surface energy and insect residue adhesion properties. The amount of FAE was varied to identify when the epoxy surface was saturated with fluorinated moieties as determined by contact angle analysis and surface energy calculations. As can be seen in Table 1, as the FAE loading is increased, indicated by the subscript following the sample name, the surface energy decreased reaching a minimum at 1 wt%. For all three test solvents, the contact angle increased and reached a plateau value, relative to measurement noise, between 0.5 and 1 wt% (data not shown). A further decrease in surface energy was achieved by incorporation of MoS_2 (Type I), SiO_2 (Type II), or a mixture thereof (Type III). The amount of filler is indicated as a subscript of the filler type in Table 1. Surface energies $< 2 \text{ mN/m}$ were calculated from the contact angle values measured on several surfaces.

Fruit flies were impacted on these surfaces and the resultant residue height and areal coverage were measured using an optical profilometer. Although no correlations were observed in previous works,⁶ minimal residue height were measured over a range of advancing water contact angle values, $\theta_{A,\text{water}}$ (Figure 2). Similar observations were made for ethylene glycol and methylene iodide data. The error associated with the insect residue heights was likely due to the impact events occurring on an airfoil substrate. Deviation in impact location, chord-wise, caused slight variation in remaining residue properties. Residue height ranges were considerably lower for flat plate impact studies (data not shown.)

A similar, though less pronounced trend was observed for the residue areal coverage and θ_A . Although not shown here, there was a linear relationship between surface roughness, R_a , and contact angle values for all three liquids. Roughness values for all surfaces measured ranged from 0.3-3.7 μm .

Table 1. Surface energy and insect impact results.

Sample	FAE wt%	Filler (wt%)	Surface Energy, mN/m	Residue Height, μm	Residue Area, mm^2
Al control	N/A	N/A	25.6	162 $\pm$ 79	0.91 $\pm$ 0.54
Epoxy	0	N/A	24.4	245 $\pm$ 31	1.27 $\pm$ 0.35
FAE _{0.1}	0.1	N/A	13.6	151 $\pm$ 75	0.72 $\pm$ 0.37
FAE _{0.5}	0.5	N/A	16.4	184 $\pm$ 47	0.96 $\pm$ 0.49
FAE ₁	1	N/A	11.8	196 $\pm$ 50	0.60 $\pm$ 0.25
FAE ₅	5	N/A	15.3	197 $\pm$ 59	0.59 $\pm$ 0.28
FAE ₁ (I ₅)	1	MoS_2 (5)	15.9	175 $\pm$ 52	0.43 $\pm$ 0.30
FAE ₁ (I ₁₀)	1	MoS_2 (10)	14	210 $\pm$ 70	0.48 $\pm$ 0.30
FAE ₁ (I ₂₅)	1	MoS_2 (25)	16.3	127 $\pm$ 66	0.48 $\pm$ 0.40
FAE ₁ (II ₅)	1	SiO_2 (5)	12.6	87 $\pm$ 77	0.07 $\pm$ 0.08
FAE ₁ (II ₁₀)	1	SiO_2 (10)	1.3	69 $\pm$ 33	0.07 $\pm$ 0.04
FAE ₁ (II ₂₅)	1	SiO_2 (25)	1	104 $\pm$ 44	0.09 $\pm$ 0.06
FAE ₁ (III ₅)	1	MoS_2 (1.25) SiO_2 (3.75)	12.6	45 $\pm$ 28	0.03 $\pm$ 0.02
FAE ₁ (III ₁₀)	1	MoS_2 (2.5) SiO_2 (7.5)	1.8	66 $\pm$ 44	0.06 $\pm$ 0.05
FAE ₁ (III ₂₅)	1	MoS_2 (6.25) SiO_2 (18.75)	0.7	145 $\pm$ 64	0.22 $\pm$ 0.10

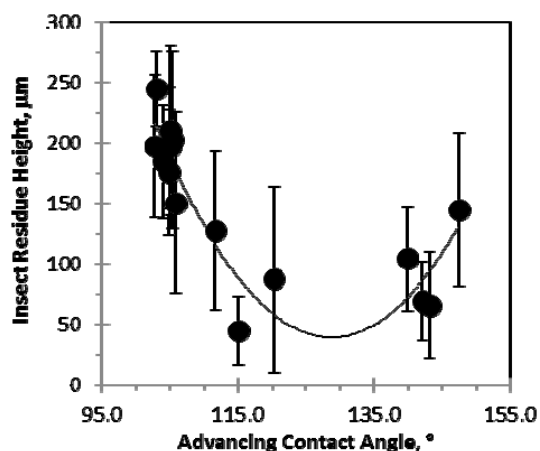


Figure 2. Observed minimum of insect residue height relative to advancing water contact angle. The line is drawn as a visual aid.

Although no correlation was observed for dispersion or total surface energy values, increasing polar surface energy values resulted in increased insect residue heights until reaching a plateau and γ_p values greater than ~ 1.5 mN/m (Figure 3).

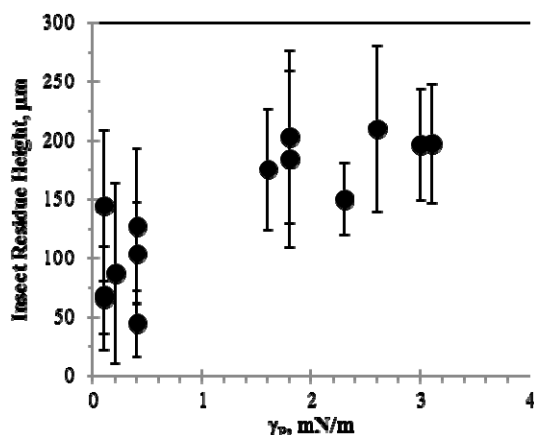


Figure 3. Increasing polar surface energy resulted in an increase in insect residue height.

The influence of filler content on insect residue areal coverage is shown in Figure 4. Incorporation of MoS₂ resulted in a slight decrease in areal coverage which did not change significantly as MoS₂ loading was increased. SiO₂-containing samples exhibited a dramatic decrease in areal coverage that was also not significantly dependent on loading level. When both fillers were incorporated, a greater reduction in areal coverage was observed with increased filler actually reducing the efficacy of the coating. Similar trends were observed for the insect residue height data.

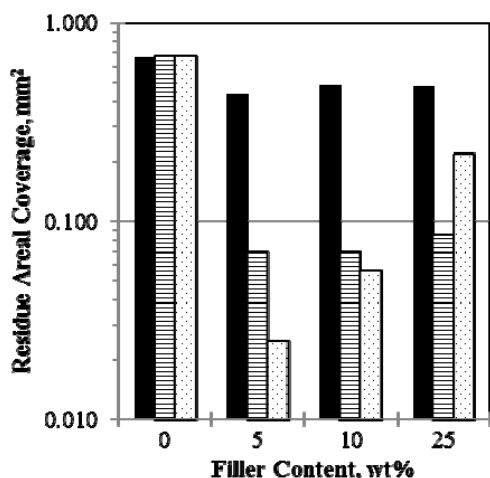


Figure 4. Areal coverage on epoxy-nanocomposite surfaces at different filler loading levels for MoS₂ (solid), SiO₂ (horizontal pattern), and a mixture of the two (dotted pattern).

Based on these results, optimal advancing contact angle ranges were identified to be: water, 115-140°; ethylene glycol, 95-135°; methylene iodide, 90-135°. Similarly,

optimal roughness values, R_a , were determined to be 1.0-3.0 μm . Additional surface compositions will be fabricated within these ranges to further explore the nature of the filler composition on insect residue adhesion properties.

Conclusions

Although none of the surfaces exhibited insect residue adhesion properties in line with the desired objective of complete residue elimination, the optimal θ_A ranges, surface roughness ranges, and γ_p relationship for the FAE-containing epoxy composites investigated here provide some insight on the influence of surface chemistry and surface roughness on performance in these tests. The notable change in adhesion properties of the MoS₂/SiO₂ combinations was unexpected and indicates a potential synergism that warrants further investigation. The lack of strong correlations between the measured surface properties and insect adhesion indicates that these surface properties are not the sole factor determining insect residue adhesion interactions.

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